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Ruhr-University Bochum, Germany, 10–13 August 2007
Pasteur Institute, France, 30 November 2007

Scope of Research

Structure and dynamics of a variety of ionic and nonionic solutions of physical, chemical, and biological interests are systematically studied by NMR and computer simulations from ambient to extreme conditions. High pressures and high temperatures are employed to shed light on microscopic controlling factors for the structure and dynamics of solutions. Static and dynamic NMR of endocrine disruptors, anesthetics, peptides, and proteins in model and cell membranes are also investigated.

Research Activities (Year 2007)

Presentations

Free Energy of Solvation in the Energetic Perspective, Matubayasi N, Multiscale Dynamics of Biomolecules 2007, Taipei, Taiwan, 13–14 April 2007.

Free Energy of Solvation in the Energetic Perspective, Matubayasi N, International Mini-Symposium on Liquids, Okayama, Japan, 11 May 2007.

Free Energy of Solvation in the Energetic Perspective, Matubayasi N, ICCMSE (International Conference of Computational Methods in Sciences and Engineering), Yokohama, Japan, 25–30 September 2007.

Solution Chemistry of Supercritical Water through Development of High-Temperature NMR Spectroscopy and Solution Theory, Matubayasi N, Joint Conference of JMLG/EMLG Meeting 2007 and 30th Symposium on Solution Chemistry of Japan, Fukuoka, Japan, 21–25 November 2007.

Anion-field Effect on Rotational Dynamics of Water and Benzene in Ionic Liquids: 1-Butyl-3-methylimidazolium Chloride and Hexafluorophosphate, Wakai C, The 2nd International Congress on Ionic Liquids (COIL-2), Yoko-

hama, Japan, 5–10 August 2007.

Structure and Dynamics of Molecules and Ions in Room-Temperature Ionic Liquids, Wakai C, Post Symposium of JMLG/EMLG Meeting 2007, Kyoto, Japan, 26 November 2007.

Grants

Nakahara M, Free-Energy Analysis of Nanoscale Aggregates of Molecules in the Method of Energy Representation, National Research Grid Initiative Project, 1 April 2003–31 March 2008.

Nakahara M, Development of Technology for Hydrogen Production, Storage, and Transportation of Hydrogen Using Hydrothermal Reactions of Formic Acid, ENEOS Hydrogen Trust Fund, 1 October 2006–30 September 2007.

Matubayasi N, Molecular Theory of the Solvation Effect on the Structural Formation and Fluctuation of Biomolecules and their Aggregates, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2003–31 March 2008.

Wakai C, NMR Study on Dynamics of Water Molecule, Organic Molecules, and Ions in Ionic Liquids, Grant-in-

Solvation Shell Dynamics Studied by Molecular Dynamics Simulation in Relation to the Translational and Rotational Dynamics of Supercritical Water and Benzene

The solvation shell dynamics of supercritical water is analyzed by molecular dynamics simulation with emphasis on its relationship to the translational and rotational dynamics. The relaxation times of the solvation number (τ^S), the velocity autocorrelation function (τ^D), the angular momentum correlation function (τ^J), and the second-order reorientational correlation function (τ^{2R}) are studied at a supercritical temperature of 400 °C over a wide density region of 0.01–1.5 g cm⁻³. The relaxation times are decomposed into those conditioned by the solvation number n , and the effect of the short-ranged structure is examined in terms of its probability P_n of occurrence. In the low to medium-density range of 0.01–0.4 g cm⁻³, the time scales of water dynamics are in the following sequence,

$$\tau^D > \tau^S \geq \tau^J \geq \tau^{2R} \quad (1)$$

This means that the rotation in supercritical water is of the “in-shell” type while the translational diffusion is not (see Figure 1). The comparison to supercritical benzene is also performed and the effect of hydrogen bonding is examined. The water diffusion is not of the in-shell type up to the ambient density of 1.0 g cm⁻³, which is corresponding to the absence of the transition from the collision to the Brownian picture, whereas such transition is present in the case of benzene. The absence of the transition in water comes from the fast reorganization of the hydrogen bonds and the enhanced mobility of the solvation shell in supercritical conditions.

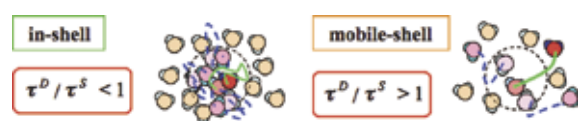


Figure 1. Schematic draw for the difference between in-shell and mobile-shell diffusions.

Rotational Dynamics of Water and Benzene Controlled by Anion Field in Ionic Liquids. 1-Butyl-3-methylimidazolium Chloride and Hexafluorophosphate

The rotational correlation time (τ_{2R}) is determined for D₂O (polar) and C₆D₆ (apolar) in 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) and hexafluorophosphate ([bmim][PF₆]) by measuring ²H (D) nuclear magnetic resonance spin-lattice relaxation time (T_1) in the temperature range from –20 to 110 °C. The τ_{2R} ratio of water to benzene ($\tau_{W/B}$) was used as a measure of solute-solvent attraction. The $\tau_{W/B}$ is 0.73 and 0.52 in [bmim][Cl] and [bmim][PF₆], respectively, whereas the molecular volume ratio is as small as 0.11. The slowdown of the water dynamics compared to the benzene dynamics in ionic liquids is interpreted by the Coulombic attractive interaction between the polar water molecule and the anion. As for the anion effect, the rotational dynamics of water solvated by Cl⁻ is slower than that solvated by PF₆⁻, whereas the rotational dynamics of benzene is similar in the two ionic liquids (see Figure 2). This is interpreted as an indication of the stronger solvation by the anion with a larger surface charge density. The slowdown of the water dynamics via Coulombic solvation is actually significant only at water concentrations lower than ~9 mol dm⁻³ at room temperature, and it is indistinguishable at temperatures above ~100 °C. The quadrupolar coupling constants determined for D₂O and C₆D₆ in the ionic liquids were smaller by a factor of 2–3 than those in the pure liquid state.

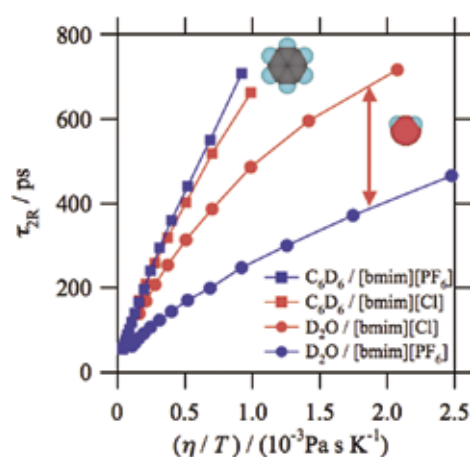


Figure 2. Plots of the rotational correlation times τ_{2R} for D₂O and C₆D₆ in ionic liquids against the solvent viscosity divided by temperature η/T .

Aid for Scientific Research on Priority Areas, 1 April 2006–31 March 2008.

Award

Matubayasi N, Award for Distinguished Achievement, The Japan Association of Solution Chemistry, 31 July 2007.